

Revealing the anomalous excited state behavior of the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex through the investigation of suitably modified ligands

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The ability of certain molecular systems to rapidly switch between two magnetic (spin) states is a unique phenomenon that may contribute to the continuing rapid improvement of the speed and storage capacity of digital storage devices or molecular switches. The basic polypyridil Fe(II) complexes are prime examples of these so-called photoswitchable spin-state transition molecules. For most of these complexes the excited state lifetimes are in the subnanosecond range at room temperature. A notable exception is the $[\text{Fe}(\text{terpy})_2]^{2+}$ with the tridentate terpy ligands, for which the excited state lifetime is significantly longer, and can even be made metastable under suitable conditions (host lattice, low temperature).^[1,2] It is believed that the long lifetimes are a consequence of the complexity of the transition process, where a single configuration coordinate is not sufficient to describe the process, and the involvement of more modes leads to an enhanced barrier to the relaxation.^[1,3] This system and its analogues are studied intensively both theoretically and experimentally.^[5,6,7,8] Explaining the anomalous behavior of the $[\text{Fe}(\text{terpy})_2]^{2+}$ complex is essential for a thorough understanding of the mechanism of the switching process, and to provide insights for an improved design of functional molecules.

With this goal in mind, aided by quantum chemical calculations and chemical intuition, we have designed and synthesized suitably modified variants of the terpy ligand, and their homoleptic complexes with Fe^{2+} . The excited state behaviour of these complexes has been investigated in solution using transient optical absorption spectroscopy, in part in our very recently constructed pump-probe setup at the Wigner Research Centre for Physics (Budapest). The substitutions on the ligand had an impact not only on the quintet excited state lifetimes, but also on the oscillations observed in the first picosecond.^[7,9] The findings, contrasted to DFT/TD-DFT calculations, provide us with detailed insights into the transitions that follow the photoexcitation. An improved understanding of this system can lead to a better control of tailoring the photophysical behaviour of similar systems. The interplay of experiments and theoretical calculations should enable us to design novel functional molecules with high potential for advanced applications.

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References:

1. A. Hauser *et al.*, *Coord. Chem. Rev.*, **2006**, 250, 1642
2. F. Renz *et al.*, *Angew. Chem. Int. Ed.*, **2000**, 39, 3699

3. M. Pápai, G. Vankó *et al.*, *J. Chem. Theor. Comput.*, **2013**, 9, 509
4. G. Vankó *et al.* *J. Phys. Chem. C*, **2015**, 119, 5888
5. X. Zhang *et al.*, *J. Phys. Chem. C*, **2015**, 119, 3312
6. J. Nance *et al.*, *Inorganic Chemistry*, **2015**, 54, 11259
7. Y. Liu *et al.*, *Chem. Commun.*, **2013**, 49, 6412
8. L. L. Jamula, J. K. McCusker *et al.*, *Inorg Chem.*, **2014**, 53, 15
9. C. Consani *et al.*, *Angew. Chem. Int. Ed.*, **2009**, 48, 7184